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**REMARKS**

The Examiner's Office Action of July 12, 2005 has been received and carefully reviewed. Applicant would like to thank the Examiner for the consideration given to the above-identified application, and Applicant notes with appreciation the indication of allowance of claims 6, 8, 10, and 11.

Prior to this Amendment, claims 6, 8, 10, 11, 18-20, 22 and 39-44 were pending. By this amendment, claims 18-20, 22 and 43-44 have been cancelled, and new claims 45-50 have been added. Accordingly, claims 6, 8, 10-11, 39-42 and 45-50 are pending for consideration in the present application, of which claims 6, 8, 10-11, 39-42 and 45-50 are independent. In view of these actions and the following remarks, reconsideration and withdrawal of these objections and rejections are respectfully requested.

Applicants enclose a copy of the LePage article and the Chemical abstract cited in the Information Disclosure Statement filed 22 April 2005 as the Examiner requested a legible copy of each reference to comply with 37 CFR 1.98(a)(2).

Referring now to the detailed Office Action, the Examiner objected to the disclosure because of alleged informalities, specifically with respect to a formula (ii) of page 3, lines 4-15, asserting that  $(A_{1-x}B_x)_yCu_zO_w$  and  $(A_{1-x}B'_x)_yCu_zO_{w'}$  can be rewritten as  $(A_{2-x-x'}B_xB'_x)_{y+y'}Cu_{z+z'}O_{w+w'}$ , which requires a minimum of 4 alkaline earth elements since it teaches B and B' are two or more alkaline earth elements each, has a value of  $y+y'$  in the range of 4-8 and has a  $w+w'$  in the range of 8-20. Furthermore, the Examiner asserted that it is unclear how  $YbBaSrCu_3O_{6-8}$ ,  $YBaCaCu_3O_{6-8}$ ,  $YbBa_{0.7}Sr_{0.7}Ca_{0.6}Cu_3O_{6-8}$ ,  $Y_{0.5}Yb_{0.5}BaSrCu_3O_{6-8}$  and  $Y_{0.5}Yb_{0.5}BaCaCu_3O_{6-8}$  of lines 18-21 on page 3 are examples of formula (ii). The Examiner also asserted that how formula (ii) is a subspecies of formula (i),  $(A_{1-x}B_x)_yCu_zO_w$ , since the amounts of A, B, copper and oxygen are at least twice as much as that of  $(A_{2-x-x'}B_xB'_x)_{y+y'}Cu_{z+z'}O_{w+w'}$ . The Examiner objected that the y and y' values of Examples 1-6 are outside the ranges of y and y' for the formula (ii) and Examples 6 and 9 teach niobium as a part of the A element, when niobium is not a rare earth element as required by the specification.

In response, Applicants amended the disclosure to correct the informalities and improve the clarity of the claim language. The formula (ii) now recites, among other features,

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"each of B and B' is one ore more alkaline earth elements." The formula (ii) on lines 5-15 on page 3,  $(A_{1-x}B_x)_yCu_zO_w \cdot (A_{1-x'}B'_{x'})_{y'}Cu_{z'}O_{w'}$ , is directed to a chemical reaction mixture of  $(A_{1-x}B_x)_yCu_zO_w$  and  $(A_{1-x'}B'_{x'})_{y'}Cu_{z'}O_{w'}$ , not a simple mathematical addition of two formulas,  $(A_{2-x-x'}B_xB_{x'})_{y+y'}Cu_{z+z'}O_{w+w'}$  as the Examiner asserted in the Office Action. Therefore,  $(A_{1-x}B_x)_yCu_zO_w$  and  $(A_{1-x'}B'_{x'})_{y'}Cu_{z'}O_{w'}$  can NOT be rewritten as  $(A_{2-x-x'}B_xB_{x'})_{y+y'}Cu_{z+z'}O_{w+w'}$ . Instead, the formula (ii) should be read as a superconducting material of a chemical reaction mixture of  $A_{(1-x)y}B_{xy}Cu_zO_w$  and  $A_{(1-x')y'}B_{x'y'}Cu_{z'}O_{w'}$  wherein each formula  $A_{(1-x)y}B_{xy}Cu_zO_w$  or  $A_{(1-x')y'}B_{x'y'}Cu_{z'}O_{w'}$  having one rare earth element and one or more alkaline earth elements, or more than one rare earth element and one or more alkaline earth elements. Accordingly, total earth element is either one or more and total alkaline earth elements are two or more. Furthermore, the range of x, y, z, and w should not be added to the range of x', y', z' and w'.

The formula (ii),  $(A_{1-x}B_x)_yCu_zO_w \cdot (A_{1-x'}B'_{x'})_{y'}Cu_{z'}O_{w'}$ , is a subspecies of the formula (i)  $(A_{1-x}B_x)_yCu_zO_w$  disclosed on page 2, lines 12-25, as both formulas are directed to a superconducting ceramic material in which B is more than one alkaline earth element when A is one rare earth elements or B is one or more alkaline earth elements when A is more than one rare earth element.

Applicants correct the clerical and/or typographical errors in EXAMPLES of the disclosure. In particular, the values of x', y and y' in EXAMPLES 1, 2 and 4, x of EXAMPLE 4 as well as y in EXAMPLE 7 were corrected to the values which is claimed in the formula (ii) of the specification. "Nb (niobium)" in EXAMPLES 6 and 9 was corrected to Nd (neodymium), which is one of rare earth elements claimed in the specification. These changes should not be considered as introducing new matter.

Therefore, the withdrawal of this objection is respectfully requested.

Claims 6, 8, 10 and 11 are rejected under 35 U.S.C. §112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which Applicant regards as the invention. Specifically, the Examiner asserted that the claimed specific formulas of  $YbBaSrCu_3O_{6.8}$ ,  $YbBa_{0.7}Sr_{0.7}Ca_{0.6}Cu_3O_{6.8}$ ,  $Y_{0.5}Yb_{0.5}BaSrCu_3O_{6.8}$  and  $Y_{0.5}Yb_{0.5}BaCaCu_3O_{6.8}$  do not fall within the claimed general formula because the formula can be rewritten as  $(A_{2-x-x'}B_xB_{x'})_{y+y'}Cu_{z+z'}O_{w+w'}$ . The Examiner stated that the formula required

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the presence of at least four alkaline earth elements, where  $0.1 \leq x+x' < 2$ ,  $y+y'=5-6$ ,  $z+z'=3-7$  and  $w+w'=12-16$ .

In response, claims 6, 8, 10 and 11 are amended to improve the clarity of the claim language. Claims 6, 8, 10 and 11 now recite, among other features, "each of B and B' is one or more alkaline earth elements." As discussed above, the formula,  $(A_{1-x}B_x)_yCu_zO_w \cdot (A_{1-x'}B'_{x'})_yCu_zO_w$  of claims 6, 8, 10 and 11 is directed to a superconducting ceramic which is a chemical reaction mixture of  $(A_{1-x}B_x)_yCu_zO_w$  and  $(A_{1-x'}B'_{x'})_yCu_zO_w$ . Therefore,  $(A_{1-x}B_x)_yCu_zO_w$  and  $(A_{1-x'}B'_{x'})_yCu_zO_w$  can NOT be rewritten as  $(A_{2-x-x'}B_xB'_{x'})_{y+y'}Cu_{z+z'}O_{w+w'}$  as the Examiner asserted in the Office Action by a simple mathematical addition of two formulas. The formula  $(A_{1-x}B_x)_yCu_zO_w \cdot (A_{1-x'}B'_{x'})_yCu_zO_w$  should be read as a superconducting material of a chemical reaction mixture of  $A_{(1-x)y}B_{xy}Cu_zO_w$  and  $A_{(1-x')y'}B'_{x'y'}Cu_zO_w$  wherein each formula  $A_{(1-x)y}B_{xy}Cu_zO_w$  or  $A_{(1-x')y'}B'_{x'y'}Cu_zO_w$  having one rare earth element and one or more alkaline earth elements, or more than one rare earth element and one or more alkaline earth elements. Accordingly, total earth element is either one or more and total alkaline earth elements are two or more. Furthermore, the range of x, y, z, and w should not be added to the range of x', y', z' and w'. Therefore, the withdrawal of this rejection with respect to claims 6, 8, 10 and 11 is respectfully requested.

Claims 18, 19, 20, 22, 43 and 44 are rejected under 35 U.S.C. § 103(a) as being unpatentable over U.S. patent 6,630,425 in view of U.S. Patent 6,635,603 and U.S. Patent 6,638,894. In response to the rejections, and in the interest of expediting the allowance of this application, Applicant has cancelled rejected claims 18, 19, 20, 22, 43 and 44 as shown above, without prejudice or disclaimer to the subject matter disclosed therein. Applicant reserves the right to file a divisional application to claim the subject matter of the cancelled claims. Accordingly, the rejections of claims 18, 19, 20, 22, 43 and 44 are rendered as moot.

Claims 39-44 are rejected under 35 U.S.C. § 112, first paragraph, as containing subject matter which was described in the specification in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention. The Examiner further asserted that claims include new matter because the claimed definitions covers embodiments where A, A', B and B' is the specified element in combination with any other element besides rare elements and alkaline earth elements.

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In response, claims 39-42 are amended to include the limitations of rare earth element and alkaline earth element. Claims 39-42 now recite, among other features, "wherein A is one rare earth element, and each of B and B' is one or more alkaline earth elements." Claims 43-44 have been cancelled. Therefore, the withdrawal of this rejection with respect to claims 39-42 is respectfully requested.

New claims 45-50 have been added to further complete the scope of the invention to which Applicant is entitled. The Examiner indicated on page 6 of the Office Action that the cited art of record do not teach ceramics having the formula  $\text{YbBaSrCu}_3\text{O}_{6-8}$ ,  $\text{YbBa}_{0.7}\text{Sr}_{0.7}\text{Ca}_{0.6}\text{Cu}_3\text{O}_{6-8}$ ,  $\text{Y}_{0.5}\text{Yb}_{0.5}\text{BaSrCu}_3\text{O}_{6-8}$  and  $\text{Y}_{0.5}\text{Yb}_{0.5}\text{BaCaCu}_3\text{O}_{6-8}$ . Therefore, Applicants add claims reciting  $\text{YbBaSrCu}_3\text{O}_{6-8}$ ,  $\text{YbBa}_{0.7}\text{Sr}_{0.7}\text{Ca}_{0.6}\text{Cu}_3\text{O}_{6-8}$ ,  $\text{Y}_{0.5}\text{Yb}_{0.5}\text{BaSrCu}_3\text{O}_{6-8}$  and  $\text{Y}_{0.5}\text{Yb}_{0.5}\text{BaCaCu}_3\text{O}_{6-8}$ . Furthermore, the Examiner noted that there is no teaching or suggestion in the cited art to replace all of Y in the formulas with Yb. Applicants add claims reciting  $\text{Yb}_{0.5}\text{Gd}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{6-8}$  and  $\text{Yb}_{0.5}\text{Nd}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{6-8}$ . The support for claims 45-50 can be found in the specification and no new matter has been added.

In view of the arguments set forth above, Applicant respectfully requests reconsideration and withdrawal of all the pending rejections.

While the present application is now believed to be in condition for allowance, should the Examiner find some issue to remain unresolved, or should any new issues arise, which could be eliminated through discussions with Applicant's representative, then the Examiner is invited to contact the undersigned by telephone in order that the further prosecution of this application can thereby be expedited.

Respectfully submitted,



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Room-temperature structure of the 90-K bulk superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{8-x}$ 

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The 90-K superconducting phase of Y-Ba-Cu-O has been isolated, and its structure at room temperature determined by single-crystal x-ray diffraction. The material is an oxygen-defect perovskite, with composition  $\text{YBa}_2\text{Cu}_3\text{O}_{8-x}$ . Entire planes of oxygen atoms between copper atoms are missing from the perovskite structure. The result is a quasi-two-dimensional structure in which sandwiches of  $\text{Ba}_2\text{Cu}_3\text{O}_{8-x}$  are separated by layers of Y.

In the first reports of superconductivity above 90 K in the Y-Ba-Cu-O system<sup>1</sup> and the first confirmations in other laboratories,<sup>2,3</sup> only a small fraction of the material, which contained several phases, was superconducting. We have prepared the pure form of this superconductor. It is a bulk superconductor and has a Meissner signal 25% of that expected for complete flux exclusion. We have determined the structure at room temperature using single-crystal x-ray diffraction and identify the compound as an oxygen-defect perovskite  $\text{YBa}_2\text{Cu}_3\text{O}_{8-x}$ . (At the conclusion of this work, we received a paper from Cava *et al.*,<sup>4</sup> where the superconducting phase was identified as  $\text{YBa}_2\text{Cu}_3\text{O}_{8-x}$  and in which the powder x-ray diffraction pattern was indexed; the lattice parameters found there are within 0.3% of ours.)

Samples of average composition  $\text{Y}_x\text{Ba}_{3-x}\text{Cu}_3\text{O}_8$  ( $x=0$  to  $x=1.5$  in steps of 0.15) were prepared from appropriate amounts of  $\text{BaCO}_3$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{CuO}$ , all 99.999% pure. The powders were mixed, then heated in alumina crucibles in air at 560°C for 24 h, 720°C for 24 h, and 960°C for 12 h. The powder x-ray diffraction patterns (determined in the Bragg-Brentano geometry with  $\text{Cu K}\alpha$  radiation) show that all the compounds except  $x=0$  have a common phase. The compound  $\text{Y}_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_8$  is almost entirely this phase, the compound  $\text{Y}_{1.20}\text{Ba}_{1.80}\text{Cu}_3\text{O}_8$  has slightly more impurities, and the other compounds have more impurities still. Energy-dispersive x-ray spectroscopic analysis in transmission electron spectroscopy of over 20 powder particles in the compound  $\text{Y}_{1.20}\text{Ba}_{1.80}\text{Cu}_3\text{O}_8$  gave the same relative composition of Y:Ba:Cu to within 2%.

The ac magnetic susceptibility per volume, measured by a mutual inductance technique, was larger for  $\text{Y}_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_8$  below 90 K than for any of the other samples. For that material, the dc magnetic susceptibility was measured with a superconducting quantum-interference device (SQUID) magnetometer on a sample cooled in a field (Meissner effect) and warmed in a field after cooling in zero field (shielding effect); the results are shown in Fig. 1. The Meissner signal is 25% of that expected for a bulk superconductor with the mass of the sample and the crystallographic density of 6.37 g/cm<sup>3</sup>. The width of the transition is comparable to that seen in our previous measurements on mixed-phase samples.<sup>2</sup>

Unlike in our previous results, however, there was no evidence of a magnetic anomaly at low temperatures.

No superconducting transition was seen in the resistivity of powders pressed into a pellet, as measured using standard four-terminal techniques as in Ref. 5. After the

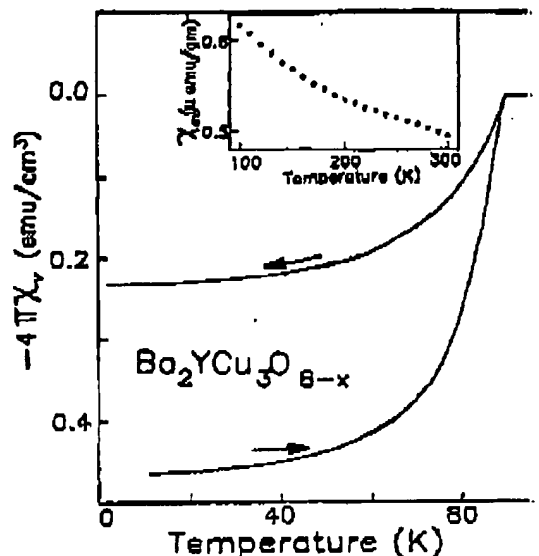


FIG. 1. Magnetic susceptibility per volume, as measured using dc susceptibility vs temperature for sample of nominal composition  $\text{Y}_{1.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_8$ , in a magnetic field of 10 G. Multiplying by  $4\pi$  gives the susceptibility as a fraction of that expected for a bulk superconductor of the same volume as the pellet. The volume was determined from the mass and the crystallographic density. As indicated by the arrows, the upper curves are for cooling in a field (Meissner effect) and the lower curves are for warming in a field after cooling in zero field (shielding effect). Our thermometers lagged behind the sample temperature by several degrees near 90 K, and we have shifted the two curves in horizontally so that the onsets lie at the average melt temperature of 90 K. The inset shows the susceptibility per unit mass in the normal state.

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pellets were sintered in air at 860 °C for 19 h, however, the resistivity did go to zero, with an onset temperature of 92 K, a midpoint of 85 K, and zero resistance at 78 K. This transition is broader than in our previous work,<sup>2</sup> where the material was grown in peller form, but only 1% of the sample was superconducting according to the Meissner effect. Thus the broad resistive transition here is probably due to poorly sintered links between the powder grains.

The powder from the sample of nominal composition  $Y_{1.20}Ba_{1.80}Cu_2O_{7-x}$  was examined for single crystals. A microscopic examination showed the existence of two phases: a dominant phase with metallic luster and a few grains of a transparent emerald-green phase, both with sizes of about 30  $\mu m$ . Although the samples of the green phase turned out to be multiple crystals, we could observe the diffraction angles for their intense x-ray reflections, and find a pseudo-orthorhombic cell indexing them. This allowed the removal of the weak impurity lines from the powder diffraction pattern. Further structural work on this phase is in progress. The similarity of the remaining lines with the perovskite structure type was obvious.

A  $40 \times 30 \times 15$  ( $\mu m$ )<sup>3</sup> crystal of the metallic phase was selected. Its diffractions could be indexed on the basis of a primitive tetragonal cell with edges approximately  $1 \times 1 \times 3$  times the cube edge of perovskite. The diffraction intensities were measured with graphite-monochromatized Mo K $\alpha$  radiation up to 50° Bragg angle, using profile analysis. Standards were measured every 100 reflections and showed no significant fluctuation apart from counting statistics. A total of 418 reflections were measured. They indicated the Laue class  $4/mmm$  with diffraction symbol  $P---$ , leaving five possibilities for the space-group symmetry:  $P422$ ,  $P4mm$ ,  $P42m$ ,  $P4m2$ , and  $P4/mmm$ . The measured intensities were corrected for absorption of x rays by Gaussian integration ( $\mu = 284.4 \text{ cm}^{-1}$ ). Data reduction with this diffraction symbol gave 133 unique

reflections. From these, 101 reflections had a net intensity larger than 2.5 $\sigma$  and were considered to be observed. The average relative deviation of individual measurements from the mean was 6.6%, reflecting the irregular mosaic spread and the imprecise face measurement. The cell parameters measured on the single crystal indicated a slight orthorhombic distortion of cell parameters, but a tetragonal distribution of intensities. Comparison with the powder pattern gave an agreement on diffraction angles and reflection intensity. In addition, the Kikuchi lines in the (001) zone pattern of transmission electron diffraction patterns do not have a fourfold symmetry, indicating an orthorhombic structure. In the following, we assume quasitetragonal cell parameters. We performed the analysis in the orthorhombic cell also with essentially identical results.

The fairly large intensities of low-angle superstructure reflections indicated that the superstructure was not exclusively displacive in nature. It had to include occupation of equivalent sites of perovskite by atoms with large differences in numbers of electrons. The starting composition of the material  $Y_{1.20}Ba_{1.80}Cu_2O_{7-x}$  and the common coordinations of Ba, Y, and Cu by O suggested a Ba<sup>2+</sup> ordering, with only one Y atom per cell. Assuming the centrosymmetric space group  $P4/mmm$ , Y had to be on one of the four Wyckoff positions with multiplicity 1. For positioning the first atom, these sites are equivalent, and we arbitrarily selected to locate Y in the middle of the cell. We then located the other atoms at ideal perovskite positions with the octahedral sites occupied by three Cu and the remaining cubo-octahedral sites (12 neighbors) occupied by two Ba atoms. Although the initial structure factor calculation gave a 48% residual, the refinement of the metal-atom positions and the oxygen positions converged quickly, with a large shift for the Cu (2) atom with refinable  $x$  parameter (Table 1). Occupancy refinement showed that one of the oxygen sites was now empty, with

TABLE I. Crystal data for  $YBa_2Cu_3O_{7-x}$ , with  $x$  refined as 1.0(4). The space group is  $Pmmm$ , quasi- $P4/mmm$ ,  $Z = 1$ . The calculated density 6.37 g/cm<sup>3</sup>; the edges of unit cell are  $a = 3.827(1)$ ,  $b = 3.877(1)$ ,  $c = 11.709(6)$  Å. Three unique sets of reflections were measured up to 50° at 298 K, with MoK $\alpha$  radiation (wavelength = 0.70932 Å), on a crystal  $40 \times 30 \times 15$   $\mu m$ . A Gaussian absorption correction was performed, giving minimum and maximum transmission factors 0.44 and 0.68. There were 133 unique measurements, of which 101 were considered observed (intensity greater than 2.5 $\sigma$ ). Residuals were  $R_f = 6\%$  on observed,  $R_i = 8\%$  on all unique structure factors, with all structure factors weighted equally. All nonoxygen atoms were refined anisotropically. The table gives the multiplicity of each site, the atomic parameters (fractional coordinates)  $X$ ,  $Y$ , and  $Z$ , as well as  $B_{iso}$  in the quasispace group  $P4/mmm$ , and the values of  $X$ ,  $Y$ , and  $Z$  for the ideal perovskite structure. ( $B_{iso}$  is the mean of the principal axes of the thermal ellipsoid.) Estimated standard deviations (in parentheses) refer to the last digit printed.

	Mult.	Refined				Ideal		
		$X$	$Y$	$Z$	$B_{iso}$	$X$	$Y$	$Z$
Y	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.7(3)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
Ba	2	$\frac{1}{2}$	$\frac{1}{2}$	0.1873(4)	0.51(15)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
Cu(1)	1	0	0	0	0.9(4)	0	0	0
Cu(2)	2	0	0	0.3558(10)	0.3(3)	0	0	$\frac{1}{2}$
O(1) <sup>a</sup>	2	0	$\frac{1}{2}$	0	4.2(10)	0	$\frac{1}{2}$	0
O(2)	4	$\frac{1}{2}$	0	0.3807(24)	0.2(6)	$\frac{1}{2}$	0	$\frac{1}{2}$
O(3)	2	0	0	0.155(6)	1.6(13)	0	0	$\frac{1}{2}$

<sup>a</sup>The refined occupancy of this atom is 0.5(2). The other sites are consistent with full occupancy.

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TABLE II. Important metal-oxygen distances. Estimated standard deviations (in parentheses) refer to the last digit printed. The number multiplying the distance indicates the number of oxygen atoms at this distance.

Y—O(2)	2.38(2) × 8	Cu(1)—O(1)	1.928(1) × 4
Ba—O(1)	2.923(3) × 4	Cu(1)—O(3)	1.81(7) × 2
Ba—O(2)	2.98(2) × 4	Cu(2)—O(1)	1.949(1) × 4
Ba—O(3)	2.75(1) × 4	Cu(2)—O(3)	2.36(7) × 1

eight oxygen atom sites remaining in the triple perovskite cell to balance one Y, two Ba, and three Cu atoms. The final residuals are  $R_f = 6\%$  on the 101 observed reflections, and 8% on the 133 unique reflections, observed and unobserved. The important distances to oxygen are given in Table II.

Although this structure is topologically closely related to perovskite, the removal of one oxygen atom per triple cell has dramatic consequences on the stereochemistry in this well-known structure type. The eliminated atom was part of two types of coordination polyhedra. It was at a shared corner between two  $\text{CuO}_4$  octahedra, shielding the two Cu atoms from one another and keeping them at a distance equal to twice the Cu—O bond length, i.e., about

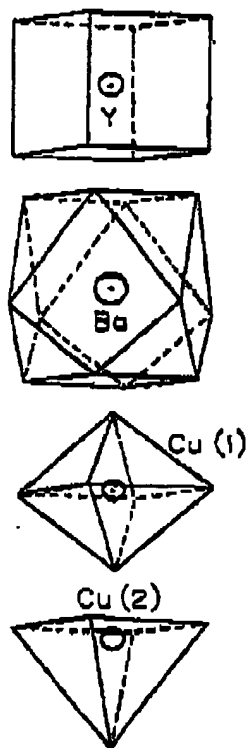


FIG. 2. The individual polyhedra of the structure  $\text{YBa}_2\text{Cu}_3\text{O}_{6-x}$ . O atoms are located at each vertex of the polyhedra.

3.8 Å, the perovskite cube edge. It was also a sixfold neighbor in the cubo-octahedron around Y. Its removal without further effects should have left around Y a trigonal prism with edge ratio equal to the square root of 2. However, the traction exerted by Y pulling on its eight oxygen neighbors to produce a smaller site to fit its lone radius combined with the lack of repulsion at the former Cu—O contact, compresses the central perovskite unit by about 1 Å along c. The above tetragonal prism becomes a nearly perfect cube. Although the now-facing Cu(2) atoms retreat perceptibly inside the tetragonal pyramids formed by the removal of one oxygen atom from their coordination octahedron, the Cu—Cu distance decreases to 3.38 Å with apparently no anion to shield them.

The disappearance of an essential oxygen site may be complete, or simply partial, corresponding to oxygen vacancy ordering. We assume full occupancy of all anion sites, which is well indicated by the refinement. Barium and yttrium can only be  $\text{Ba}^{2+}$  and  $\text{Y}^{3+}$ , and Cu can take valence 1+ or 2+, and occasionally 3+. Due to the oxidizing experimental conditions, valence 1+ is unlikely. The number of oxygen atoms balancing the formula should be 6.5 if Cu is in the 2+ state and 8 if Cu is in the 3+ state. Occupancy refinement of oxygen sites indicates that sites O(2) and O(3) are fully occupied, while site O(1) is about 50% occupied. The refined formula is therefore  $\text{YBa}_2\text{Cu}_3\text{O}_{6-x}$  with x approximately equal to 1, indicating that the overall Cu valency is intermediate between 2 and 3.

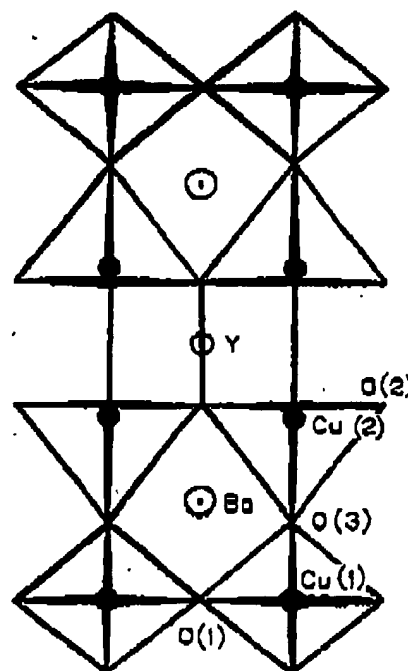


FIG. 3. The projection of the stacking down a. The atoms are located at the vertices of the polyhedra.

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The perovskite structure type is therefore barely recognizable here, and the coordination polyhedra follow: Cu(1), an octahedron of the 2+4 type with average Cu-O distance 1.89 Å; Cu(2) a square pyramid corresponding to 4+1 coordination; Ba a perceptibly elongated cuboctahedron; and finally, Y occupies a cube with Y-O distance 2.38 Å. All these distances are fairly typical of the species found in the site and corroborate the initial chemical assignments. Figure 2 illustrates the individual polyhedra and Fig. 3 their stacking projected down a.

In the superconductors  $\text{La}_{2-x}\text{M}_x\text{CuO}_{4-y}$  ( $M = \text{Sr}, \text{Ba}, \text{Ca}$ ) there are two-dimensional layers of Cu-O separated by M and O.<sup>2,8</sup> Here there are sandwiches of  $\text{Ba}_2\text{Cu}_2\text{O}_{7-2x}$  separated by layers of Y. The partially occupied oxygen sites, which may also have a large thermal motion, are located in the center of these sandwiches. As in  $\text{La}_{2-x}\text{M}_x\text{CuO}_{4-y}$ , this two-dimensional aspect may be a key to the high superconducting transition temperature observed in this material. Our work clarifies the room-

temperature stereochemistry of the 90-K superconducting phase, but important questions pertaining to the precise behavior of anions in the planes  $x=0$  and  $x=\frac{1}{2}$  have not been answered. This will require larger and better crystals, which should be simpler to produce now that the stereochemistry is known.

*Note added in proof.* We believe the single crystal studied here and all the other crystals we have seen since are domain crystals, so we could not detect an ordering of the O atoms in the partially occupied O1 sites. That ordering has been observed by powder neutron diffraction by Gredan, O'Reilly, and Stager [Phys. Rev. (to be published)]; they find the oxygen atoms occupy the O1 sites along b but not those along a.

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**DETAILED RESULTS:**

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TITLE: Development of a superconductor material at 92 K from a single-phase yttrium-barium-copper-oxygen ceramic

INVENTOR(S): Morato, Spero Penha; Baldochi, Sonia Licia

PATENT ASSIGNEE(S): Instituto de Pesquisas Energeticas e Nucleares (IPEN), Brazil

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AB A material which is superconductive at 92 K is prepd. by heating a mixt. of Y2O3, BaCO3, and CuO in an O atmospheric at 970°C for 12-16 h and then cooled at the rate of 20° C/h. The resultant ceramic material, which has the formula YBa2Cu3O6.5, exhibited supercond. at 92 K.

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